



## Research article

## L-cysteine intercalated layered double hydroxide for highly efficient capture of U(VI) from aqueous solutions

Pengyi Wang<sup>a</sup>, Ling Yin<sup>a</sup>, Xiangxue Wang<sup>a,b</sup>, Guixia Zhao<sup>a,\*\*</sup>, Shujun Yu<sup>a,\*\*\*</sup>, Gang Song<sup>c</sup>, Jing Xie<sup>a</sup>, Ahmed Alsaedi<sup>d</sup>, Tasawar Hayat<sup>d</sup>, Xiangke Wang<sup>a,d,\*</sup><sup>a</sup> College of Environmental Science and Engineering, North China Electric Power University, Beijing 102206, China<sup>b</sup> Department of Environmental Science and Engineering, North China Electric Power University, Baoding 071003, China<sup>c</sup> Guangdong Provincial Key Laboratory of Radionuclides Pollution Control and Resources, Guangzhou 510006, China<sup>d</sup> NAAM Research Group, Faculty of Science, King Abdulaziz University, Jeddah 21589, Saudi Arabia

## ARTICLE INFO

## Article history:

Received 17 October 2017

Received in revised form

11 March 2018

Accepted 25 March 2018

## Keywords:

Layered double hydroxide

L-cysteine

U(VI)

Adsorption

Interaction mechanism

## ABSTRACT

L-cysteine intercalated Mg/Al layered double hydroxide (Cys-LDH) composites were fabricated and applied for treating the U(VI) contaminated wastewater under various conditions. Interaction mechanisms and adsorption properties were investigated by using batch experiments with spectroscopy analysis. The adsorption isotherms and kinetics were fitted perfectly with the Langmuir isotherm and the pseudo-second-order model, respectively. The significant maximum adsorption capacity of Cys-LDH (211.58 mg/g) compared to LDH was attributed to the larger number of functional groups on Cys-LDH. The presence of humic acid (HA) decreased U(VI) elimination on Cys-LDH at high pH but increased U(VI) removal at low pH. Typically, the presence of various anions (such as NO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>, ClO<sub>4</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup>) did not obviously affect U(VI) adsorption on Cys-LDH, while the coexisted CO<sub>3</sub><sup>2-</sup> significantly affected U(VI) elimination. The predominate adsorption were determined to be the formation of Cys-U(VI)-Cys complexes with cysteine in the Cys-LDH interlayers. The results demonstrated that the Cys-LDH are promising adsorbents for efficient elimination and extraction of radionuclides in actual environmental contamination management.

© 2018 Elsevier Ltd. All rights reserved.

## 1. Introduction

With the extensively application of nuclear industries, the environmental pollution and human health crises caused by radionuclides are receiving more attention (Sun et al., 2016a). Especially for actinides with a long half-life, radionuclides can cause a long-term radioactive hazard for the surrounding water environment and human health, even at low concentrations (Panak et al., 2013). For example, uranium, one of the essential nuclear energy sources, with high solubility and a long radioactive half-life, has been identified as an environmental radioactive pollutant in minerals, sea water and soils (Chen et al., 2017). Meanwhile, uranium-

containing wastewater from uranium mining and nuclear fuel activities is unavoidable discharged into the natural surroundings, where it can pose a strong radioactive effect and profound toxicity threat for ecological system and human beings (Ma et al., 2015; Zou et al., 2017a). Therefore, the efficient removal and recovery of radionuclides from polluted water have been investigated intensively. Adsorption is one of the cost-effective and convenient methods to remove the radionuclides from wastewater because of its simple operation in large scale (Fang et al., 2017; Peng et al., 2017). Various adsorbents such as clay minerals (Zou et al., 2017a), metal (hydr)oxides (Sun et al., 2016b; Yu et al., 2017), metal-organic framework (Li et al., 2018) and carbon-based materials (Sun et al., 2017; Yu et al., 2016d) have been applied to eliminate radionuclides. However, a number of issues, such as low adsorption capacity and removal efficiency of clay minerals, as well as a high-cost of carbon-based materials, have limited the application of these adsorbents in full-scale environmental pollution remediation. Therefore, it is an urgent issue to explore low-cost adsorbents with high elimination capacity.

\* Corresponding author. College of Environmental Science and Engineering, North China Electric Power University, Beijing 102206, China.

\*\* Corresponding author.

\*\*\* Corresponding author.

E-mail addresses: [guixiazhang@techchem.rub.de](mailto:guixiazhang@techchem.rub.de) (G. Zhao), [sjy@ncepu.edu.cn](mailto:sjy@ncepu.edu.cn) (S. Yu), [xkwang@ncepu.edu.cn](mailto:xkwang@ncepu.edu.cn) (X. Wang).

Layered double hydroxide (LDH), one of the well-known and extensively studied anionic clays with positively charged host layers and negatively charged interlamination anions, has shown excellent anion-exchange and intercalation properties (Mallakpou et al., 2014; Yao et al., 2017; Yu et al., 2017). These characteristics allow LDH to be used as adsorbents (Wen et al., 2013), catalysts (Varga et al., 2016), and scavengers and nanoreactors in multidisciplinary applications (Mallakpou et al., 2014). To obtain novel LDH or its derivatives with high surface areas, large interlamellar spaces and abundant functional groups, an intercalation modification method has been widely applied to enhance the adsorption capacity of LDH (Ma et al., 2015). It is well known that  $\text{UO}_2^{2+}$  is the most stable species in aqueous solutions, and it can easily form covalent bonds with  $\text{S}^{2-}$ -containing groups (Ma et al., 2015; Manos et al., 2012). In recent investigations, Wang et al. (2016a) reported that the maximum amount of U(VI) adsorption by prismatic sulphides was 127 mg/g. Similarly, Ma et al. (2015) found that polysulfide modified LDH exhibited significant removal efficiency for U(VI) elimination from wastewater due to the  $\text{S}^{2-}$ -containing groups on the LDH surface could enhance the elimination capacity of LDH. L-cysteine (Cys) is a water soluble and non-essential amino acid that contains many functional groups, including a sulfhydryl group ( $-\text{SH}$ ), carboxyl group ( $-\text{COOH}$ ), and amino group ( $-\text{NH}_2$ ) (Ashour et al., 2016; Loganathan et al., 2015). In Cys molecules,  $-\text{NH}_2$  and  $-\text{COOH}$  are the two basic functional groups, while  $-\text{SH}$  is the exclusive group that exhibits strong binding capacity to  $\text{UO}_2^{2+}$  ions (Ashour et al., 2016). Therefore, Cys might be a desirable modification or intercalation material for LDH to improve its adsorption capacity.

Herein, we prepared Cys-LDH via intercalating Cys molecules into Mg/Al-LDH interlayers and then applied Cys-LDH for removing  $\text{UO}_2^{2+}$  from aqueous solutions. The prepared Cys-LDH was characterized by powder X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), and Fourier transformed infrared spectroscopy (FT-IR). The effects of co-existing ions, temperature, contact time and humic acid on the adsorption of  $\text{UO}_2^{2+}$  were explored to investigate interaction mechanisms and speculate on the possibility of Cys-LDH use in wastewater treatment.

## 2. Materials and method

### 2.1. Materials

L-cysteine (Cys), magnesium nitrate hexahydrate ( $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ), uranium nitrate ( $\text{UO}_2(\text{NO}_3)_2$ ), aluminium nitrate nonahydrate ( $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ) and other chemical reagents were purchased as analytical-grade and used without any further purification. Humic acid (HA) was extracted from soil samples from the Hua-Jia countryside (Gansu Province, China) and was characterized in our previous studies (Yu et al., 2016c; Zhao et al., 2011).

### 2.2. Synthesis of nanostructured Mg/Al-LDH and Cys-LDH composites

The nanostructured Cys-LDH and Mg/Al-LDH were prepared via a simple one-pot coprecipitation method (Wei et al., 2007). Generally, a sufficient amount of Cys (0.003 mol) was added to 30 mL NaOH solutions ( $\text{pH} = 10.5 \pm 0.1$ ) and stirred for 5 min. Subsequently, a 20-mL solution with  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (9 mmol) and  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (3 mmol) was added into the Cys-containing alkaline solution under vigorous stirring under ambient condition. The pH of suspension was adjusted to 10.5 by adding 4 mol/L NaOH under continuous stirring for 30 min, and then aged for 12 h at 80 °C. The precipitates were washed with ethanol and Milli-Q water

three times, and then in the obtained suspension were transformed to a vacuum at 60 °C for 8 h. For comparison, the pure Mg/Al-LDH was prepared with identical procedure without the addition of Cys.

### 2.3. Characterization techniques

XRD patterns and FT-IR spectra of as-prepared Cys-LDH and Mg/Al-LDH before and after U(VI) adsorption were obtained on a Philips X'Pert Pro Super X-ray diffractometer (Agilent, USA) using  $\text{Cu-K}\alpha$  radiation ( $\lambda = 0.154$  nm) and a Nicolet IR spectrometer (Shimadzu, Japan), respectively. TEM element mapping images were obtained by using a JEOL-2010 (Shimadzu, Japan) microscopy. SEM images and energy dispersive spectra (EDS) were obtained by using a Hitachi S-4800 microscope (Hitachi, Japan). XPS spectra were measured with a ESCALab220i-XL electron spectrometer (Shimadzu, Japan). The Brunauer-Emmett-Teller (BET) surface area was measured by  $\text{N}_2$  adsorption-desorption isotherms (Quantachrome Ins., USA). The distribution of U(VI) as a function of pH at different environment was simulated by Visual MINTEQ software.

### 2.4. Batch adsorption experiments

The batch experiments of U(VI) adsorption on Mg/Al-LDH and Cys-LDH were conducted by using 10 mL polyethylene tubes. The suspensions of Cys-LDH or Mg/Al-LDH (4 g/L), U(VI) (240 mg/L) in  $\text{NaNO}_3$  solution (1 mol/L, the background electrolyte) were mixed in to achieve the expected concentrations. The solution pH values were adjusted negligible amounts of different concentrations of NaOH or  $\text{HNO}_3$ . After shaking for 24 h, the U(VI) concentration in supernatant was measured by using Arsenazo-III method at 650 nm in UV-2550 spectrophotometry (Shimadzu, Japan). The adsorption capacity ( $q_e$ , mg/g), the distribution coefficient ( $K_d$ ) and removal percentage (Removal, %) were calculated from the following equations:

$$\text{Removal}(\%) = \frac{C_0 - C_e}{C_0} \times 100\% \quad (1)$$

$$q_e = (C_0 - C_e) \times \frac{V}{m} \quad (2)$$

$$K_d = \frac{C_0 - C_e}{C_e} \times \frac{V}{m} \quad (3)$$

where  $C_e$  (mg/L) and  $C_0$  (mg/L) were U(VI) concentration after adsorption equilibration, and U(VI) initial concentration, respectively.  $V$  (mL) and  $m$  (g) were the volume of the suspension and the mass of adsorbent, respectively. Relative errors of 5% were allowed in all experimental measurements.

## 3. Results and discussion

### 3.1. Characterization

The microstructures of samples were observed by SEM images. As shown in Fig. 1a and b, the two materials all exhibited a regular hexagonal structure (Ma et al., 2016). TEM elemental mapping (Fig. 1c and d) demonstrated the homogeneous distribution of Mg, Al and O in Mg/Al-LDH structures, and Mg, Al, O, N and S in Cys-LDH structures, which indicated that the Cys molecules were incorporated into the Mg/Al-LDH structures (Wei et al., 2006). The EDS spectra of as-prepared Mg/Al-LDH and Cys-LDH (Fig. S1) also revealed the existence of Mg, Al, and O in Mg/Al-LDH and the existence of S, O, N, Mg and Al in Cys-LDH. In addition, the atomic

Download English Version:

<https://daneshyari.com/en/article/7477458>

Download Persian Version:

<https://daneshyari.com/article/7477458>

[Daneshyari.com](https://daneshyari.com)